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(54) **PRODUCTION OF ION EXCHANGER**

(57) Abstract:

PURPOSE: To obtain an ion exchanger whose ionic permeability, especially, permselectivity among ions of the same charges can be varied, by polymerizing an oxidatively polymerizable monomer in an ion exchanger containing an oxidizing agent.

CONSTITUTION: An oxidatively polymerizable monomer is polymerized in an ion exchanger containing an oxidizing agent. As the ion exchanges, not only organic ion exchangers but also inorganic ion exchangers themselves such as zirconium phosphate and those

formed by molding these inorganic ion exchangers by application of pressure and heat with the aid of a suitable organic or inorganic binder can be used. Examples of said oxidizing agents include peroxides such as H_2O_2 and $(C_6H_5CO)_2O_2$, metal salts such as $FeCl_3$ and $CuSO_4$, peroxy acids (salts) such as $Na_2S_2O_8$ and Na_2SO_5 and oxy-acid salts such as $NaClO$ and $NaBrO$. Examples of the oxidatively polymerizable monomers which can be particularly desirably used include pyrrole, indole, azulene, thiophene, furan and their derivatives.

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⑰ 発明の名称 イオン交換体の製造方法

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明 細 書

1. 発明の名称

イオン交換体の製造方法

2. 特許請求の範囲

1) 酸化剤を含有するイオン交換体中で酸化重合可能な単量体の重合させることを特徴とするイオン交換体の製造方法。

3. 発明の詳細な説明

(産業上の利用分野)

本発明は酸化剤を含有するイオン交換体中で酸化重合可能な単量体を重合させるイオン交換体の製造方法に関する。

(従来技術および問題点)

従来、イオン交換膜の機能としてイオン選択透過性を向上させたり、低下せしめたり、両符号イオン間の選択透過性を変えるために、種々の方法が試みられてきた。さらにイオン交換膜に新しい機能と試みするための種々の試みとして、重合可能なビニル単量体を陽イオン交換膜、或いは陰イオン交換膜中に含浸重合させる方法が行われ、塩

の低透過量の減少、塩率の向上、膜の漏洩量の減少、塩素の漏洩量の減少をもたらしってきた。しかし、これらの方法は一般にビニル単量体を膜内で重合させる場合が多く、イオン交換膜自体がこれらのビニル単量体によって膨潤することがあるため、膜の機械的強度の低下を招く問題がある。また、縮合系の単量体をイオン交換膜内で重合させることも報告されているが、縮合反応を完結させるために、加熱処理を必要とする場合が多く、膜の性能を損う問題が生ずる。

(問題点を解決するための手段)

本発明者らは上記に鑑み、広く一般にイオン交換体のマトリックス中に別ポリマーのマトリックスを形成することによって、該イオン交換体の特性を変え、また該イオン交換体に新しい機能と試みることが出来ないか種々検討を重ねた。その結果、ピロール及びその誘導体、チオフェン及びその誘導体などの複素環化合物がイオン交換体に対して親和性がよく、且つ酸化反応によって比較的容易に膜内で重合し、該イオン交換体の特性が

変わり、また新たに有用な機能を有するイオン交換体が得られることを見出して、本発明を提供するに至ったものである。即ち、本発明によれば、酸化剤を含有するイオン交換体中で酸化重合可能な単量体を重合させることを特徴とするイオン交換体の製造方法が提供される。

本発明のイオン交換体としては有機系イオン交換体に限らず、例えばリン酸ジルコニウム等の無機イオン交換体そのもの、及びこれらを適当な有機、無機の結合剤によって加圧・加熱成型したものも好適に用いられる。有機系のイオン交換体としては重合系のイオン交換体、即ちスチレン・ジビニルベンゼン系の共重合体でイオン交換基が結合したもの、縮合等のイオン交換体で陽イオン交換基及び／または陰イオン交換基を結合したものが好適に用いられる。かかるイオン交換体としては従来公知の均一系、不均系のイオン交換体を用いることも出来、また該イオン交換体の基体として炭化水素系のもの、あるいは炭素系のもの、パーフルオロカーボン系のものの如何に関係なく、好

適に同時に存在する場合も含まれる。同時に存在する場合は二種のイオン交換基が二層以上に亘って層状に存在する場合、任意に均一に存在する場合のいずれでもよい。また、陽イオン交換基が存在する層があり、陽イオン交換基と陰イオン交換基が任意に分布する層があり、再び陽イオン交換基が存在する層がある場合、或いは陰イオン交換基を有する層が存在する層がある場合、或いはこれの逆の場合など各種のイオン交換基の存在状態によって各種のイオン交換体が形成されるが、これら全ての形態のイオン交換体がそれぞれ本発明の方法において有効に適用される。なお、上記した陽イオン交換基および陰イオン交換基は、同一種類の陽イオン交換基、陰イオン交換基を意味するのではなく、例えばカルボン酸基とスルホン酸基といった異なった陽イオン交換基であってもよいが、異種のものを用いたとき、特に有効である場合が多い。また、上記した無機イオン交換体、有機イオン交換体はそれぞれ単独のマトリックスのものに限定されるのではなく、両者の複合体も

適に用いられる。

また、本発明に用いられるイオン交換体は、乾燥した該イオン交換体の1gあたり一般に0.1~1.5ミリ当量のイオン交換基を結合しているものであれば特に限定されない。そのイオン交換基としては従来公知の陽イオン交換基であるスルホン酸、カルボン酸、リン酸、亜リン酸、スルホン酸エステル、フェノール性水酸基、チオール基、三級のパールオロアルコールなどが用いられ、陰イオン交換基としては一級、二級、三級アミン、第四級アンモニウム、第三級スルホニウム、第四級ホスホニウム、コバルチラニウム等のオニウム塩基が好適である。

また、上記したイオン交換体としては、イオン交換基が基体に均一に分散しているもの、一方に片寄って存在しているもの、濃度勾配が存在するものなど各種のものが必要に応じて好適に用いられる。このようなイオン交換体に存在するイオン交換基は陽イオン交換基のみが存在する場合、陰イオン交換基のみが存在する場合、両イオン交換

基が同時に存在する場合、好適に用いられる。具体的には、無機イオン交換体の酸粉体を熱可塑性の有機イオン交換体によって成型して適当な形状としたもの、或いは適当な溶媒に高分子電解質または不活性な高分子を溶解し、これに無機イオン交換体を分散させて溶媒を飛散させることにより、必要とする形状のイオン交換体とすることが出来る。さらに、本発明に用いるイオン交換体は、膜状物の他に、粒状物、粉状物、繊維状物、管状物など各種の形状のものが用いられる。

本発明においては、上記した如き各種のイオン交換体を用いて、かつ後記する酸化剤および酸化重合可能な単量体を選択することにより、それぞれ改良された有用なイオン交換体を得ることが出来る。以下、その略略的な態様を記す。例えば、
(1) 陰イオン交換体に対して陽イオンの酸化剤、また陽イオン交換体に対して陰イオンの酸化剤を用いることにより、それぞれイオン交換体に酸化剤が均一に含有され離れ点を利用して、片側のみ酸化重合可能な単量体を容易に重合できるため、

非対称構造のイオン交換体を得ることが出来る。

(2) これに対して、两性イオン交換体を用いる場合には、陽イオンおよび陰イオンのいずれの酸化剤も均一に含有されるために、酸化重合可能な単量体を重合して均一構造のイオン交換体を容易に得ることが出来る。(3) また、パイポーラー形のイオン交換膜を用いる場合には、片面だけに酸化重合可能な単量体を重合できるため、該重合体の電導性層に絶縁性層とを交互に有する膜状物質を得ることが出来る。(4) 架橋構造を有する炭化水素系のイオン交換体を用いる場合には、酸化重合可能な単量体の含有速度、含炭量がコントロールし易いために、得られるイオン交換体の機械的強度を保持し易い利点がある。特に、架橋構造と共に補強材を有するイオン交換体を用いる場合には、より機械的強度を有するイオン交換体を得ることが出来る。

本発明において、イオン交換体中に存在させる酸化剤としては、従来公知の酸化剤であれば特に限定されない。例えば、 H_2O_2 、 $(C_2H_5CO)_2O_2$ などの

として N-メチルピロール、2-エチルピロールなど、チオフェン及びその誘導体、イソシアナタテン及びその誘導体、インドール、アズレン、フラン、アニリン、フェノール、ベンゼン、ナフタリン等のそれぞれの誘導体があげられる。特にピロール、インドール、アズレン、チオフェン、フランおよびそれらの誘導体など複素環化合物は、イオン交換体に対して親和性が高く、該イオン交換体に容易に酸化重合するため、好適に用いられる。

本発明における酸化重合の方法は特に限定的でなく一般に酸化剤を含有するイオン交換体を有機溶媒、例えばアセトニトリル、エチルアルコール、或いは無機系の溶媒、例えば水中に酸化重合可能な単量体を溶解、或いは分散した中に浸漬すればよい。浸漬は溶媒が凍結しない範囲での冷却下、或いは溶媒が沸騰しない範囲での加熱下に行われる。また、重合において、単量体の濃度は特に限定的でなく 0.01% から単量体の飽和溶媒までよく、懸濁状態で重合させてもよい。重合時間は単量体

過酸化物、 F_2C_2 、 $CuSO_4$ 、 $CuCl_2$ 、 $RuCl_3$ などの金属塩、 $Na_2S_2O_8$ 、 Na_2SO_5 、 $(NH_4)_2SO_5$ などのペルオクソ酸(塩)、 $NaClO$ 、 $NaBrO$ 、 $NaClO_3$ などの酸素酸塩などが挙げられる。即ち、三価の鉄イオン、二価の銅イオン、三価のルテニウムイオンなどの荷電が酸化還元によって変化する金属イオン、同様に荷電が酸化還元によって変化する有機化合物あるいは金属錯体陽イオンなどの陽イオン類、また過硫酸イオン、過塩素酸イオンなどの酸化性を有する陰イオンが好適に用いられる。これら陽イオン及び陰イオンは、酸化状態でイオン交換体の交換基とイオン交換しイオン交換体内に均一に分散するので好適である。なお、イオン交換体の表面部のみにおいて、本発明の酸化重合反応を興発したときには、長鎖アルキル基を結合した過酸、或いはナフタリン環のようなイオン交換体の細孔内に容易に入り得ないような化合物に過酸基が結合したようなものを用いることが出来る。

本発明において、用いられる酸化重合可能な単量体としては、例えばピロールおよびその誘導体

の種類、イオン交換体の種類によって変わり、一般に 1 分以上、72 時間までの適当な時間を選定して行うことが出来る。

(発明の作用、効果)

本発明で得られるイオン交換体はイオンの透過性、特に同符号イオン間の選択透過性が変わり、一般に電荷の大きいイオン種、水和イオン半径の小さいイオン種の透過が阻止されるようになる。また、単量体の酸化重合の方法によっては、電子伝導性の機能が賦与されて、イオン交換膜がセンサーなどの新しい機能性物質に変わることになる。

以下に若干の具体的な例を示す。

- (1) ステレン-ジビニルベンゼンで架橋した陽イオン交換膜を塩化鉄の水溶液中に浸漬して鉄イオン型にしたのち、これを充分に水洗し、ピロールを含む水溶液中に浸漬すると、ピロールは陽イオン交換すると同時に重合する。このようにして得られた膜を充分に水洗し、1 規定の塩酸と 0.5 規定の食塩水で充分にコンタクションゲルして Fe^{3+} を除去したのち、0.25 規定の塩酸と

非対称構造のイオン交換体を得ることが出来る。(2) これに対して、两性イオン交換体を用いる場合には、陽イオンおよび陰イオンのいずれの酸化剤も均一に含有されるために、酸化重合可能な単量体を重合して均一構造のイオン交換体を容易に得ることが出来る。(3) また、パイポーラー形のイオン交換膜を用いる場合には、片面だけに酸化重合可能な単量体を重合できるため、該重合体の電導性層に絶縁性層とを交互に有する膜状物質を得ることが出来る。(4) 架橋構造を有する炭化水素系のイオン交換体を用いる場合には、酸化重合可能な単量体の含浸速度、含浸量がコントロールし易いために、得られるイオン交換体の機械的強度を保持し易い利点がある。特に、架橋構造と共に補強材を有するイオン交換体を用いる場合には、より機械的強度を有するイオン交換体を得ることが出来る。

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過酸化物、 $FeCl_3$ 、 $CuSO_4$ 、 $CuCl_2$ 、 $RuCl_3$ などの金属塩、 $Na_2S_2O_8$ 、 Na_2SO_5 、 $(NH_4)_2SO_5$ などのペルオクソ酸(塩)、 $NaClO$ 、 $NaBrO$ 、 $NaClO_3$ などの過酸塩などが挙げられる。即ち、三個の鉄イオン、二個の銅イオン、三個のルテニウムイオンなどの荷電が酸化還元によって変化する金属イオン、同様に荷電が酸化還元によって変化する有機化合物あるいは金属錯体陽イオンなどの陽イオン類、また過硫酸イオン、過塩素酸イオンなどの酸化性を有する陰イオンが好適に用いられる。これら陽イオン及び陰イオンは、酸化状態でイオン交換体の交換基とイオン交換しイオン交換体内に均一に分散するので好適である。なお、イオン交換体の表層部のみに於いて、本発明の酸化重合反応を実施したいときには、長鎖アルキル基を結合した過酸、或いはナフタリン環のようなイオン交換体の細孔内に容易に入り得ないような化合物に過酸基が結合したようなものを用いることが出来る。

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以下に若干の具体的な例を示す。

- (1) ステレン-ジビニルベンゼンで架橋した陽イオン交換膜を塩化鉄の水溶液中に浸漬して鉄イオン膜にしたのち、これを充分に水洗し、ピロールを含む水溶液中に浸漬すると、ピロールは陽イオン交換すると同時に重合する。このようにして得られた膜を充分に水洗し、1規定の塩酸と0.5規定の食塩水で充分にコンディショニングして Fe^{3+} を除去したのち、0.25規定の塩酸と

例に於いても同様にした。

実施例 2

エチレン、ジビニルベンゼンおよび4-ビニルピリジンの混合物にポリ塩化ビニル微粉末を添加し、次いで重合開始剤であるベンゾイルパーオキサイドを加えて粘稠なペースト状混合物とし、これをポリ塩化ビニル製の布に塗布し、両面をセラフアンでおおい、70℃に窒素雰囲気中で加熱重合して高分子膜状物を得た。これをヘキサンおよびヨウ化メチルの混合溶液からなるアルキル化溶媒に25℃で24時間浸漬して、第4級アンモニウム塩基を陰イオン交換基とする陰イオン交換膜を得た。

この陰イオン交換膜を過硫酸アンモニウムの10%水溶液中に浸漬して過硫酸イオン型にイオン交換膜を交換した後、これを5%のアニリンを分散した水溶液中に浸漬し室温で8時間撈拌した。膜状物は淡黄色から黒変した。

これを取り出して、1規定の塩酸と0.5規定のアンモニウム水でコンディショニングした後、0.25

ヨウ化メチルからなる溶媒に浸漬してピリジン環をアルキル化処理した。このようにして得た両性イオン交換膜の陽イオン交換容量は0.51ミリ当量/平方乾燥膜で、陰イオン交換容量は1.12ミリ当量/平方乾燥膜であった。この両性イオン交換膜を用いて次の二つの処理を行った。

- (a) 三塩化ルテニウムの水溶液中に膜を浸漬して膜をルテニウムイオン型に変換し、次いで水洗乾燥した後、2%のピロール水溶液中に浸漬したところ、両性イオン交換膜中にピロールが含浸重合した。水洗、メタノール洗浄後、減圧乾燥して、電導度を測定したところ電気抵抗 $2.5 \Omega\text{-cm}^2$ であった。
- (b) 過硫酸ソーダの5%水溶液中に浸漬して過硫酸イオン型にしたのち、アニリンの1%水溶液中に撈拌下に浸漬して重合させ、これを水洗、メタノール洗浄して後、減圧乾燥したところ、 $19 \Omega\text{-cm}^2$ の電導度を示した。

尚、いづれの膜も0.25規定の塩酸と0.25規定の食塩の1:1の混合溶液の電気透析を実施したと

規定の芒硝と0.25規定の食塩との1:1の混合溶液を実施例1と同様に電気透析して、 SO_4^{2-} と Cl^- の膜透過性を比較した。その結果、アニリンを含浸重合していない膜は Cl^- 1当量の透過に対して0.3当量の SO_4^{2-} が透過したが、アニリンを膜内で重合した膜では SO_4^{2-} が0.01当量しか膜透過しなかった。

尚、上記の電気透析したあとのアニリンを含浸重合した陰イオン交換膜について、減圧乾燥したのち、電導度の測定をしたところ電気抵抗 $12 \Omega\text{-cm}^2$ であった。

実施例 3

スチレン、4-ビニルピリジンおよびジビニルベンゼンの混合物にポリ塩化ビニルの微粉末を加えて得たペースト状混合物にベンゾイルパーオキサイドを加えて、これをポリプロピレン製の不織布に塗布し、加熱して重合し膜状物とした。これを97%硫酸に浸漬してゆるやかに3日間かけてスルホン化処理した。次いで、これを一旦0.1規定の苛性ソーダ中に浸漬したあと、ヘキサンとヨ

ロールを含浸重合した膜は電流効率95%で、 Na^+ 1当量に対して水素イオン2.1当量を膜透過した。また、ポリアニリンが含浸重合した膜は電流効率97%で、 Na^+ 1当量に対して水素イオン3.0当量を透過した。

実施例 4

スチレン、ブタジエンおよびN,N'-ジメチルピロベンジルアミンをリビングアニオン重合にして、ブロック共重合体を合成した。これを平板上にキャストングしてフィルムとして、電顕によって観察したところ相分離構造を形成していた。即ち、スチレンの領域、ブタジエンの領域、N,N'-ジメチルピロベンジルアミンの領域に分れていた。このフィルムを硫酸によってスルホン化してスルホン酸基を導入し、次いでメタノールで置換したのち、沃化メチルで処理して四級アンモニウム塩基を導入した。このようにして得たモザイク状に陽イオン交換基領域、中性領域および陰イオン交換基領域が分布した膜を、三塩化鉄の水溶液中に浸漬して鉄イオンを陽イオン交換基にイオン

交換させた。次いで、これをピロールの2%のブセトニトリル溶液中に浸漬したところ、主にスルホン酸基が存在する領域にピロールは含浸し酸化重合した。

上記で得た膜状物を用いて炭塩と蔗糖の透過性を測定したところ、ピロールが含浸して酸化重合していない膜は炭塩に比べて蔗糖の透過係数は $1/81$ であったのが、ピロールを含浸して酸化重合した膜の透過係数は $1/210$ に減少していた。また、同様にして作った別の膜を水洗、メタノール洗いして減圧乾燥して電導度を測定したところ、膜の厚み方向には電導性があったが、膜の二次元方向には全く電導度は無く、即ち異方導電性膜となっていた。

実施例5

スチレンとジビニルベンゼンの混合物にポリエチレンの微粉末を混合し粘稠なペースト状混合物を作り、これをポリプロピレン製の布に塗布したあと、膜の片面のみ反応できる反応装置で膜の片面のみ硫酸によってスルホン化処理して、片面

のアニリンのエタノール溶液に浸漬した。10時間後、陰イオン交換基の部分でアニリンは重合していた。この部分は電導性が認められた。

次いで、この膜を第二塩化鉄の5%水溶液中に浸漬し、陽イオン交換基の部分に鉄イオンをイオン交換し、水洗後ピロールの2%エタノール溶液に浸漬したところ、陽イオン交換基が存在する部分でピロールが重合し、水洗、減圧乾燥後の電導度を測定したところ、この面にも電導度が認められた。

実施例7

市販の陽イオン交換樹脂、陰イオン交換樹脂及び両性イオン交換樹脂にそれぞれ次の処理をした。

- (a) スルホン酸型の陽イオン交換樹脂を第二塩化鉄水溶液に平衡にしたのち、ピロールの10%水溶液に浸漬して放置したところ、やや褐色の陽イオン交換樹脂は黒色となり重合した。
- (b) 第四級アンモニウム塩基型の陰イオン交換基を有する樹脂を過硫酸アンモニウムの10%水溶液中に浸漬した後、アニリンのエタノール溶

液に浸漬して放置したところ、黒色の球状樹脂となった。

のミスルホン酸基を導入した。次いで、これを三塩化ルテニウムの5%水溶液に浸漬してルテニウムイオン型としたのち、ピロールの10%エチルアルコール溶液に16時間浸漬したところ、スルホン酸基の部分にのみピロールが含浸し酸化重合した。これを水洗、メタノール洗滌、減圧乾燥して電導度を測定したところ、膜の片面のみ二次元方向に導電性が認められ、裏面は絶縁体となっていた。

実施例6

実施例5で片面のみスルホン化した膜を再び片面のみ反応が出来る反応装置に組み込み、未反応の面にクロルメチルエーテルと四塩化スズの四塩化炭素溶液を接触させて、クロルメチル基と膜の片面に導入した。次いで、この膜をトリメチルアミンの水-アセトン溶液に浸漬してアミノ化反応を行い、膜の片面にスルホン酸基があり、裏面に第四級アンモニウム塩基のある膜を作った。この膜を過硫酸ソーダの5%水溶液中に浸漬して陰イオン交換基の部分を通硫酸イオン型に変えた後、5

液に浸漬して放置したところ、黒色の球状樹脂となった。

- (c) 第四級アンモニウム塩基とスルホン酸基を有する球状の両性イオン交換樹脂を第二塩化鉄の5%水溶液中に浸漬した後、ピロールの水溶液中に浸漬したところ、同様に球状樹脂は黒色となり、ピロールが酸化重合した。

上記したa), b), c) の樹脂のいずれも、減圧乾燥後に測定の結果、電導性が認められた。

実施例8

ポリクロロメチルスチレンをノズルから押し出して管状のポリマーを得た。これを塩化アルミニウムの二酸化炭素溶液と接触させて、フリーデルクラフト酸によって架橋反応を形成させた。次いで、これをトリメチルアミン、水およびアセトンの混合溶液に浸漬してアミノ化処理して第四級アンモニウム塩基を有する管状陰イオン交換体とした。これを過硫酸アンモニウム水溶液中で平衡にして、ピロールの水溶液中に浸漬した。

上記した管状物の電気伝導度を測定したところ、

ビローンを重合しないものは電導度は認められなかったが、ビローンを重合したものは電導度が認められた。

実施例 9

スチレンとジビニルベンゼンの共重合体をスルホン化処理して得た陽イオン交換樹脂の微粉末をポリエチレンと混合し、実施例 8 と同様にしてノズルから押出して管状の陽イオン交換体を合成した。これを一旦純水で沸騰させたあと、三塩化鉄の水溶液中に浸漬して、鉄型としたのち、これをチオフェンの 2 % 水溶液中に浸漬して、50℃に加熱して 24 時間放置した。次いで、この管状イオン交換体を取り出して、水洗、減圧乾燥して、電導度を測定したところ、電導性が認められた。

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English translation of JP 63-023933A

1. Title of the Invention

Process for Producing Ion Exchanger

2. What is Claimed is:

1) A process for producing an ion exchanger, characterized by polymerizing an oxidation-polymerizable monomer in an ion exchanger which contains an oxidizer.

3. Detailed Description of the Invention

(Industrial Applicability)

The present invention relates to a process for producing an ion exchanger polymerizing an oxidation-polymerizable monomer in an ion exchanger which contains an oxidizer.

(Prior Art and Problem)

Various methods hitherto have been tried in order to improve or lower ion-selective permeability which is one of the functions of ion-exchange membranes, or to change selective permeability between ions of the same polarity. Further, various trials have been made to impart a new function to ion exchange membranes: that is, a polymerizable vinyl monomer is incorporated and polymerized into a cation or anion ion exchange membrane to thereby decrease the amount of a diffusing and permeating salt, to improve a transport number or to decrease the leakage amount of an acid or a base. However, in most of these methods, the vinyl monomers are polymerized in the membranes, so that the ion exchange membranes are swollen by these vinyl monomers, which may lead to a decrease in

the mechanical strengths of the membranes. It is also reported that condensation type monomers are condensed in ion exchange membranes. However, in most cases, heat treatments are needed to complete the condensation reactions, which may degrade the performance of the membranes.

(Means for Solving the Problem)

Under such a situation, the present inventors have made various trials so as to impart new functions to ion exchanges by forming matrices of different polymers in the matrices of conventional ion exchangers to thereby change the features of the ion exchangers. As a result, they have found that heterocyclic compounds such as pyrrole and its derivatives, thiophene and its derivatives, etc., which show good affinity to the ion exchangers, can be polymerized in the membranes of the ion exchangers with relative ease by oxidation reaction, to thereby change the features of the ion exchangers, and to impart new and useful functions to the ion exchangers. The present invention is accomplished based on this finding. According to the present invention, there is provided a process for producing an ion exchanger, characterized by polymerizing an oxidation-polymerizable monomer in an ion exchanger which contains an oxidizer.

Examples of the ion exchanger to be suitably used in the present invention include not only organic ion exchangers but also inorganic ion exchangers such as zirconium phosphate, and ion exchangers obtained by molding these ion exchangers with the use of appropriate organic or inorganic binders under pressure and heating. As the organic ion exchangers, there are preferably used

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polymerization type ion exchangers, so-called styrene-divinylbenzene-based copolymers to which ion exchange groups are bound, or condensation type ion exchangers to which cation exchange groups and/or anion exchange groups are bound. As such ion exchangers, conventionally known homogeneous or heterogeneous ion exchangers also can be used. Also, hydrocarbons, carbon fluorides and perfluorocarbons can be preferably used as base materials of the ion exchangers, independently of the kinds thereof.

There is no limit in selection of the ion exchanger to be used in the present invention, in so far as generally 0.1 to 15 milli-equivalent of ion exchange groups are bound per 1 g of the dried ion exchanger. Preferable examples of the ion exchange group include the known cation exchange groups such as sulfonic acid, carboxylic acid, phosphoric acid, phosphorous acid, sulfonate, phenolic hydroxyl group, thiol group, tertiary perfluoroalcohol, etc.; and anion exchange groups such as primary, secondary and tertiary amines; and onium bases such as quaternary ammonium, tertiary sulfonium, quaternary phosphonium, cobaltiranium, etc.

As the above-described ion exchanger, one suitable for end use is selected from various ion exchangers such as an ion exchanger in which ion exchange groups are uniformly dispersed on a base material, an ion exchanger in which ion exchange groups are present collectively on one side, an ion exchanger which has a concentration gradient of ion exchange groups, etc. Again, such ion exchangers may have cation exchange groups alone or anion exchange groups alone, or concurrently may have both kinds of ion exchange groups. When an ion exchanger concurrently has both kinds of ion

exchange groups, the two kinds of ion exchange groups may be present in the form of two or more layers, or may be uniformly present in an optional form. There can be formed a variety of ion exchangers, according to the states of ion exchange groups present therein; for example, there is an ion exchanger which has a layer having cation exchange groups therein, a layer having cation exchange groups and anion exchange groups optionally distributed therein, and a layer having cation exchange groups therein or a layer having anion exchange groups therein; or an ion exchanger which has a structure reverse to the above structure. The process of the present invention can be effectively applied to all of these forms of ion exchangers. In this regard, the above-described cation exchange groups and anion exchange groups do not mean cation exchange groups and anion exchange groups of the same kinds but may be cation exchange groups and anion exchange groups of different kinds: that is, they may be different cation exchange groups, for example, carboxylic acid groups and sulfonic acid groups. In many cases, the use of different kinds of ion exchange groups is particularly effective. In addition, each of the above-described inorganic ion exchangers and organic ion exchangers does not necessarily have a single matrix, and composites of both of inorganic and organic ion exchangers can be preferably used. In concrete, fine particles of an inorganic ion exchanger may be molded with a thermoplastic organic ion exchanger and formed into an appropriate shape; or otherwise, an ion exchanger with a desired shape may be produced by dispersing an inorganic ion exchanger in a solution of a polymeric electrolyte or an inert polymer in an appropriate solvent, to thereby

splash the solvent. The ion exchangers to be used in the present invention may be in the forms of not only membranes but also particles, powder, fibers, tubes, etc.

In the present invention, the variety of the ion exchangers described above are used to provide improved and useful ion exchangers, by selecting oxidizers and oxidation-polymerizable monomers described below. Hereinafter, schematic embodiments thereof are described.

(1) An ion exchanger having an asymmetric structure can be provided by using a cationic oxidizer relative to an anion exchanger, or an anionic oxidizer relative to a cation exchanger, since it is hard to uniformly contain each of the oxidizers in each of the ion exchangers so that an oxidation-polymerizable monomer can be easily polymerized on one side alone of the ion exchanger.

(2) An ion exchanger having a uniform structure can be provided by using a dipolar ion exchanger, since any of a cationic oxidizer and an anionic oxidizer can be uniformly contained in the ion exchanger to polymerize an oxidation-polymerizable monomer.

(3) A membrane-like material having conductive layers of a polymer and insulating layers alternately can be provided by using a bipolar type ion exchange membrane, since an oxidation-polymerizable monomer can be polymerized in only one side thereof.

(4) An ion exchanger which is easy to maintain its mechanical strength can be provided by using a hydrocarbon type ion exchanger having a crosslinked structure, since the impregnation rate and the impregnated amount of an oxidation-polymerizable monomer can be easily controlled. In particular, an ion exchanger having a higher mechanical

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strength can be provided by using an ion exchanger which has a crosslinked structure and contains a reinforcing material.

In the present invention, the oxidizer to be contained in the ion exchanger may be any of the known oxidizers, and is not particularly limited. Examples of such oxidizers include peroxides such as H_2O_2 and $(C_6H_5CO)_2O_2$; metal salts such as $FeCl_3$, $CuSO_4$, $CuCl_2$ and $RuCl_3$; peroxyacids (salts) such as $Na_2S_2O_8$, Na_2SO_5 and $(NH_4)_2SO_5$; and salts with oxyacids such as $NaClO$, $NaBrO$ and $NaClO_3$. In other words, there are preferably used metal ions of which the charges are changed by oxidation reduction, such as trivalent iron ions, bivalent copper ions and trivalent ruthenium ions; organic compounds of which the charges are changed by oxidation reduction; cations such as metal complex cations; and anions having oxidizing property, such as persulfate ions and perchlorate ions. These cations and anions are preferable, since such cations and anions in oxidized states are exchanged with the exchange groups of the ion exchanger and thus are uniformly dispersed in the ion exchanger. To cause the oxidation polymerization of the present invention only in the surface layer of the ion exchanger, there can be used, as the oxidizer, a peracid to which long-chain alkyl groups are bound, or a compound such as a naphthalene ring which is hard to enter the pores of the ion exchanger and which has peracid groups bound thereto.

In the present invention, examples of the oxidation-polymerizable monomer include pyrrole and its derivatives such as N-methylpyrrole and 2-ethylpyrrole; thiophene and its derivatives; isothianaphthene and its derivatives; and

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indole, azulene, furan, aniline, phenol, benzene and naphthalene, and their derivatives. In particular, heterocyclic compounds such as pyrrole, indole, azulene, thiophene, furan, and their derivatives are preferable, because they show sufficient affinity to ion exchangers and are easily oxidation-polymerized to the ion exchangers.

The method of oxidation-polymerization to be employed in the present invention is not limited. For example, an ion exchanger containing an oxidizer is immersed in a solution or a dispersion of an oxidation-polymerizable monomer in an organic solvent such as acetonitrile or ethyl alcohol, or an inorganic solvent, for example, water. This immersion is carried out under cooling where the solvent is not frozen, or under heating where the solvent is not boiled. In the polymerization, the concentration of the monomer is not limited, and it is from 0.01% to a concentration for a saturated solution of the monomer. The polymerization may be carried out as suspension polymerization. The polymerization time varies depending on the type of the monomer and the type of the ion exchanger. The polymerization time is appropriately selected generally within a range of from one minutes to 72 hours.

(Operation and Effect of the Invention)

An ion exchanger obtainable in the present invention is variable in ion permeability, particularly selective permeability of ions of the same polarity, and generally inhibits permeation of ion species with large charges and ion species with small radii of hydration ions. Again, depending on the oxidation-polymerization method for the monomer, it is possible to impart an electron conductive

function to an ion exchange membrane, so that the ion exchange membrane can be used as a new functional material such as a sensor.

Some of concrete examples of such a case will be described below.

(1) A cation exchange membrane crosslinked with styrene-divinylbenzene was immersed in an aqueous solution of iron chloride so that the membrane could be of iron ion type. After that, the membrane was sufficiently rinsed with water and was then immersed in an aqueous solution containing pyrrole so that the pyrrole was exchanged with cations and was simultaneously polymerized. The resultant membrane was sufficiently rinsed with water and was sufficiently conditioned with 1N hydrochloric acid and 0.5N brine to remove Fe^{++} , and was then used for electrodialysis of a solution which contains 0.25N hydrochloric acid and 0.25N salt, so that hydrogen ions were allowed to selectively permeate the membrane.

(2) The membrane prepared in the step (1) was dried under reduced pressure, and the electric conductivity thereof was measured. As a result, the membrane showed an electric resistance of $1 \text{ k}\Omega\text{-cm}^2$ or lower. On the other hand, a membrane to which the above-described pyrrole was not polymerized had an electric resistance of $20 \text{ M}\Omega\text{-cm}^2$ or higher.

(3) An anion exchange resin having pyridinium bases as anion exchange groups was equilibrated in an ammonium persulfate solution to be of persulfate ion type, and was then immersed in an aqueous solution of pyrrole, so that the pyrrole was selectively adsorbed onto the anion exchange membrane for ion exchange and was polymerized

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thereto. The pale yellowish globular resin was turned black. The resultant polymer was not eluted even when the globular resin was repeatedly rinsed with an acid and an alkali.

(4) A tubular ion exchanger having benzyltrimethylammonium ions as anion exchange groups was equilibrated in an aqueous ammonium persulfate solution to be of persulfate ion type, and was then immersed in an aqueous solution of aniline, so that the aniline was incorporated and polymerized into the anion exchanger. The pale yellowish tubular anion exchanger was turned black. The electric conductivity of the anion exchanger was measured. As a result, it showed an electric resistance of $100 \Omega\text{-cm}^2$ or lower. On the other hand, an anion exchanger which was not impregnated with aniline showed an electric resistance of $20 \text{ M}\Omega\text{-cm}^2$ or higher.

(5) A pyridinium base type membrane-like anion exchanger was immersed in an aqueous solution of ammonium persulfate so that anion exchange groups were exchanged with persulfate ions. After that, aniline was added to the solution to be polymerized therein. As a result, the aniline was polymerized in a liquid phase to be turned into black polyaniline and concurrently to be incorporated and polymerized into the membrane-like material. The membrane-like material was removed, and the selective permeability thereof to sulfate ions and chlorine ions was measured. When polyaniline was not present in the membrane-like material, 0.3 equivalent of sulfate ions permeated the membrane-like material, when one equivalent of chlorine ions permeated the same material. On the other hand, the membrane-like material impregnated with the polyaniline

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allowed permeation of 0.01 equivalent of sulfate ions.

(Examples)

The present invention is described in more detail by way of Examples thereof, which however should not be construed as limiting the scope of the present invention in any way.

Example 1

A dry cation exchange membrane ($7.0 \times 7.0 \text{ cm}^2$) with an ion exchange capacity of 2.3 milli-equivalent/g, which had sulfonic acid groups bound thereto, was immersed in a 5% ferric chloride aqueous solution and equilibrated therein to be of ferric ion type. Sequentially, the ferric ion type membrane was immersed in a 2% pyrrole aqueous solution (500 cc) and was stirred therein. The membrane was left to stand therein for 16 hours and was then removed. The membrane was rinsed with water and washed with ethanol, and was then immersed in 1N hydrochloric acid, while hydrochloric acid being repeatedly exchanged. Absorption of the iron was observed by means of fluorescent X-ray, and almost no iron was found to be removed from the membrane.

The membrane thus obtained was built in an acrylic cell partitioned into two chambers with inner volumes of 120 cc, and the two chambers were filled with a 0.25N NaCl solution and a 0.25N CaCl_2 solution, respectively. The membrane had been sufficiently equilibrated in the 0.25N NaCl solution and the 0.25N CaCl_2 solution before it was built in the cell with the two chambers. A silver electrode and a silver chloride electrode were attached to both the chambers of the cell, respectively, to carry out electrodialysis through the electrodes at a current density of 1 A/dm^2 . The effective current-carrying area was 0.1

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dm². After 2 hours of current-carrying, the amount of cations which had permeated the membrane was determined. As a result, the current efficiency was 97%, and the amount of Ca²⁺ which had permeated the membrane was 0.2 equivalent, when one equivalent of Na⁺ had permeated the membrane.

On the other hand, a conventional sulfonic acid type cation exchange membrane which had no pyrrole incorporated and polymerized thereinto was used for comparison. This membrane was used for electrodialysis and measurement under the same conditions. As a result, the current efficiency was 98%, and the amount of Ca²⁺ which had permeated the membrane was 2.1 equivalent, when one equivalent of Na⁺ had permeated the membrane.

In the meantime, the former membrane which had pyrrole incorporated and polymerized thereinto and which had been used for the above electrodialysis was removed from the cell, and was equilibrated in 1N hydrochloric acid and was then dried under reduced pressure. After that, the electric conductivity of the membrane was measured. As a result, the electric resistance of the membrane was 28 Ω-cm². On the other hand, the latter cation exchange membrane which had no pyrrole incorporated and polymerized thereinto showed an electric resistance of 20 MΩ-cm² or higher under the same conditions.

In this connection, the cation exchange membranes used were made from a styrene-divinylbenzene copolymer, and the content of divinylbenzene was 5%. The measurement of electric conductivity was made on the membrane with a width of 1 cm on which silver paste was applied at every 1 cm interval and dried, using a conductivity meter, and a conversion was made from the thickness of the membrane to

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calculate a specific conductivity. The measurements in the following Examples were made in the same manner.

Example 2

A viscous paste mixture was prepared by admixing a mixture of ethylene, divinylbenzene and 4-vinylpyridine with fine particles of polyvinyl chloride, followed by benzoyl peroxide as a polymerization initiator. The paste mixture was applied to a polyvinyl chloride fabric, and both sides of the fabric were covered with cellophane sheets. Heat polymerization was allowed to take place at 70°C under a nitrogen atmosphere to obtain a polymeric membrane. This membrane was immersed in an alkylating bath of a solution mixture of hexane and methyl iodide, at 25°C for 24 hours, to obtain an anion exchange membrane which had quaternary ammonium bases as anion exchange groups.

This anion exchange membrane was immersed in an aqueous solution of 10% ammonium persulfate to thereby convert the type of the membrane to persulfate ion type. Then, this membrane was immersed in an aqueous dispersion of 5% aniline and was stirred at room temperature for 8 hours. The pale yellowish membrane was turned black.

The membrane was removed and was conditioned with 1N hydrochloric acid and a 0.5N aqueous ammonia solution. After that, this membrane was used for electrodialysis of a solution mixture of 0.25N mirabilite and 0.25N sodium chloride in the ratio of 1 : 1 in the same manner as in Example 1, and the permeabilities of this membrane to SO_4^{--} and Cl^- were compared. As a result, a membrane which had no aniline incorporated and polymerized thereinto allowed permeation of 0.3 equivalent of SO_4^{--} , relative to

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permeation of one equivalent of Cl^- . In contrast, the membrane which had aniline incorporated and polymerized thereinto allowed permeation of only 0.01 equivalent of SO_4^{--} .

The anion exchange membrane which had aniline incorporated and polymerized thereinto and which had been used for the above-described electrodialysis was dried under reduced pressure. Then, the electric conductivity of the membrane was measured. As a result, the membrane showed an electric resistance of $12 \Omega\text{-cm}^2$.

Example 3

A paste mixture was prepared by admixing a mixture of styrene, 4-vinylpyridine and divinylbenzene with polyvinyl chloride fine particles, followed by benzoyl peroxide. This paste mixture was applied to a polypropylene non-woven fabric and was polymerized into the fabric under heating. Thus, a membrane-like material was obtained. This material was immersed in 97% sulfuric acid so as to be gently sulfonated over 3 days. This material was once immersed in 0.1N caustic soda and was then immersed in a bath of hexane and methyl iodide to thereby alkylate the pyridine rings. The cation exchange capacity of a bipolar ion exchange membrane thus obtained was 0.81 milli-equivalent per 1 g of the dried membrane; and the anion exchange capacity thereof was 1.12 milli-equivalent per 1 g of the dried membrane. This bipolar ion exchange membrane was subjected to the following two treatments.

(a) The membrane was immersed in an aqueous solution of ruthenium trichloride to convert the type of membrane to a ruthenium ion type, and then, the membrane was rinsed with

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water and dried. After that, the membrane was immersed in an aqueous solution of 2% pyrrole, so that the bipolar ion exchange membrane had pyrrole incorporated and polymerized thereinto. This membrane was rinsed with water and washed with methanol and was then dried under reduced pressure. The electric conductivity of the dried membrane was measured. As a result, the membrane showed an electric resistance of $25 \Omega\text{-cm}^2$.

(b) The membrane was immersed in an aqueous solution of 5% sodium persulfate to convert the type of membrane to a persulfate ion type and was then immersed in an aqueous solution of 1% aniline to polymerize the aniline under stirring. The membrane was rinsed with water and washed with methanol and was then dried under reduced pressure. This membrane showed an electric conductivity of $19 \Omega\text{-cm}^2$.

Either of the membranes was used for electrodialysis of a solution mixture of 0.25N hydrochloric acid and 0.25N sodium chloride in the ratio of 1 : 1. As a result, the membrane which had pyrrole incorporated and polymerized thereinto showed a current efficiency of 95% and allowed permeation of 21 equivalent of hydrogen ions relative to permeation of one equivalent of Na^+ . The membrane which had polyaniline incorporated and polymerized thereinto showed a current efficiency of 97% and allowed permeation of 30 equivalent of hydrogen ions relative to permeation of one equivalent of Na^+ .

Example 4

A block copolymer was synthesized by living anion polymerization of styrene, butadiene and N,N'-dimethyl-vinylbenzylamine. This block copolymer was cast onto a

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flat plate to form a film. This film was observed with an electron microscope and was found to have a phase-separation structure. That is, the film had a styrene region, a butadiene region and a N,N'-dimethylvinylbenzylamine region which were separated from one another. This film was sulfonated with sulfuric acid to introduce sulfonic acid groups thereinto. Then, the film was rinsed with methanol to substitute the sulfonic acid groups, and was then treated with methyl iodide to thereby introduce quaternary ammonium bases thereinto. Thus, there is obtained a membrane in which a cation exchange group region, a neutral region and an anion exchange group region were distributed in a mosaic pattern. This membrane was immersed in an aqueous solution of iron trichloride to thereby exchange iron ions with cation exchange groups. Next, this membrane was immersed in a solution of 2% pyrrole in acetonitrile. As a result, the pyrrole was incorporated mainly in the region having sulfonic acid groups therein and was oxidation-polymerized therein.

The resultant membrane was used to measure the permeability of sodium chloride and saccharose. The region of the membrane which had no pyrrole incorporated and polymerized thereinto showed a saccharose permeability of 1/81 in comparison with sodium chloride. The region of the membrane which had pyrrole incorporated and polymerized thereinto showed a decreased saccharose permeability of 1/210. Another membrane made in the same manner was rinsed with water and washed with methanol and was then dried under reduced pressure. The electric conductivity of the resultant membrane was measured. As a result, the membrane showed electric conductivity in the thickness direction but

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showed quite none in the two-dimensional direction. That is, the membrane was found to be an anisotropic conductive membrane.

Example 5

A viscous paste mixture was prepared by admixing a mixture of styrene and divinylbenzene with polyethylene fine particles. This paste mixture was applied to a polypropylene fabric. After that, only one side of the fabric was sulfonated with conc. sulfuric acid, using a reaction device capable of reacting only one side of the fabric. Thus, the fabric had sulfonic acid groups introduced into its only one side. Then, this fabric was immersed in an aqueous solution of 5% ruthenium trichloride to convert the type of the fabric to a ruthenium ion type. Then, the fabric was immersed in a solution of 10% pyrrole in ethyl alcohol for 16 hours, so that the pyrrole was incorporated and oxidation-polymerized into only the sulfonic acid group portion. The fabric was rinsed with water and washed with methanol and was then dried under reduced pressure. The electric conductivity of the fabric was measured. As a result, the fabric showed electric conductivity in the two-dimensional direction only at its one side, and the reverse side thereof was found to be insulating.

Example 6

The membrane sulfonated at its one side, obtained in Example 5, was again set in the reaction device capable of reacting only one side of the membrane, so that the unreacted side of the membrane was brought into contact

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with a solution of tin tetrachloride and carbon tetrachloride in chloromethyl ether to thereby introduce chloromethyl groups into the one side of the membrane. Then, this membrane was immersed in a solution of trimethylamine in water and acetone to aminate the membrane. Thus, there was obtained a membrane which had sulfonic acid groups at its one side and had quaternary ammonium bases at its reverse side. This membrane was immersed in an aqueous solution of 5% sodium persulfate to convert the anion exchange group portion of the membrane into a persulfate ion type portion. This membrane was then immersed in a solution of 5% aniline in ethanol. After 10 hours had passed, the aniline was polymerized in the anion exchange group portion of the membrane. This portion of the membrane showed electric conductivity.

Next, this membrane was immersed in an aqueous solution of 5% ferric chloride, so that the cation exchange group portion of the membrane was exchanged with iron ions. The membrane was rinsed with water and was then immersed in a solution of 2% pyrrole in ethanol, so that the pyrrole was polymerized at the portion having cation exchange groups therein. This membrane was rinsed with water and dried under reduced pressure. The electric conductivity of the resultant membrane was measured. As a result, this side of the membrane also showed electric conductivity.

Example 7

Commercially available cation exchange resin, anion exchange resin and bipolar ion exchange resin were treated as follows, respectively.

(a) A sulfonic acid type cation exchange resin was

equilibrated in an aqueous solution of ferric chloride and was then immersed in an aqueous solution of 10% pyrrole and was left to stand alone. As a result, the slightly brownish cation exchange resin was turned black, and the pyrrole was found to be polymerized.

(b) A resin containing quaternary ammonium base type anion exchange groups was immersed in an aqueous solution of 10% ammonium persulfate and was then immersed in a solution of aniline in ethanol and was left to stand alone. As a result, the resin was formed into a black globular resin material.

(c) A globular bipolar ion exchange resin material which contained quaternary ammonium bases and sulfonic acid groups was immersed in an aqueous solution of 5% ferric chloride, and was then immersed in an aqueous solution of pyrrole. As a result, the globular resin material was turned black, and the pyrrole was found to be oxidation-polymerized.

Any of the above-described resins a), b) and c) was dried under reduced pressure and measured with respect to electric conductivity. As a result, any of them showed electric conductivity.

Example 8

A tubular polymer material was obtained by extrusion-molding polychloromethylstyrene via a nozzle. The tubular polymer material was brought into contact with a solution of aluminum chloride in carbon disulfide to cause a crosslinking reaction in the presence of Friedel-Crafts acid. The tubular polymer material was then immersed in a solution mixture of trimethylamine, water and acetone to be

aminated. Thus, a tubular anion exchanger containing quaternary ammonium bases was obtained. This tubular anion exchanger was equilibrated in an aqueous solution of ammonium persulfate and was then immersed in an aqueous solution of pyrrole.

The electric conductivity of the tubular anion exchanger was measured. As a result, a tubular anion exchanger having no pyrrole polymerized thereto showed no electric conductivity. On the other hand, the tubular anion exchanger having pyrrole polymerized thereto showed electric conductivity.

Example 9

A styrene-divinylbenzene copolymer was sulfonated to obtain fine particles of a cation exchange resin. The cation exchange resin fine particles were mixed with polyethylene, and the mixture was extruded from a nozzle in the same manner as in Example 8, to obtain a tubular cation exchanger. This tubular cation exchanger was once boiled in pure water and was then immersed in an aqueous solution of iron trichloride to thereby convert the type of the exchanger to an iron type one. This exchanger was immersed in an aqueous solution of 2% thiophene and was heated to 50°C and was then left to stand alone for 24 hours. After that, the tubular ion exchanger was removed and rinsed with water and was then dried under reduced pressure. The electric conductivity of the dried tubular ion exchanger was measured. As a result, the tubular ion exchanger showed electric conductivity.